

# Hierarchy of Multipolar Terms for Non Relativistic Moving Atoms in QED

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## **Abstract**

In this article an hierarchy of terms in the expansion of the multipolar Hamiltonian for non relativistic moving atoms in QED is considered. The particular case of neutral composite systems of 2,3 and 4 particles is considered. The proposed hierarchy is based on a scaling analysis of the multipolar Hamiltonian together with a multipolar expansion of the coupling terms. We give explicit results up to the fourth order in the fine structure constant.

## **1 Introduction**

The theory of multipolar Hamiltonians for atoms in QED has been mainly developped through the Power-Zienau-Wooley (PZW) transformation for the minimal coupling Hamiltonian. This formulation is well suited for the description of a confined system of charges and is particularly relevant for a neutral system where the vector potential disappears. For moving atoms there have been few proposals of such Hamiltonians [H, LBBL,GR] owing to the fact that, up to the first order in the fine structure  $\alpha$ , symetries of the  $p \cdot A$  and  $d \cdot E$  schemes are the same. Higher order terms has been discussed mostly in the framework of two level systems [LBBL, W], and more

recently for real atoms [BBB]. The analysis of usually disregarded terms [GR] appeals for a systematic procedure that can lead to an unambiguous hierarchy of the terms in the multipolar expansions in order to perform a relevant perturbation theory. In this note we focus on QED of moving non relativistic light atoms, without external fields. These atoms are composite systems of two, three or four particles in order to make explicit the role of the increasing complexity of the problem. The point is to examine how the scaling technique performed from the beginning can be associated with multipolar expansions in order to obtain a straightforward hierarchy of terms in the Hamiltonian. The second section reviews the QED multipolar Hamiltonian and the relevant physical quantities, the third section presents a sketch of the scaling technique and proposes a way to determine which terms are predominant in the Hamiltonian and the fourth section makes a direct use of that choice within the multipolar expansion of the interaction terms and gives also the corresponding expansion for the minimal coupling Hamiltonian. Finally, in the fifth section, the use of Jacobi coordinates is introduced and explicit expansions are given.

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## 2 The multipolar Hamiltonian

We consider a neutral system of  $N$  charges  $(e_a)_{1 \leq a \leq N}$ , with masses  $(m_a)_{1 \leq a \leq N}$ , spins  $(S_a)_{1 \leq a \leq N}$  and Landé coefficient  $(g_a)_{1 \leq a \leq N}$ . The PZW Hamiltonian for QED in Coulomb gauge is given by (see [GR]):

$$H_{mp} = \sum_{a=1}^N \frac{1}{2m_a} \left( p_a + \int \Theta_a(r) \wedge B(r) d^3r \right)^2 + \sum_{a < b} \frac{e_a e_b}{4\pi\epsilon_0 |r_a - r_b|} - \sum_{a=1}^N M_a \cdot B(r_a) + \frac{1}{2} \int d^3r \left( \frac{(\Pi(r) + P(r))^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right), \quad (1)$$

with

$$p_a = -i\hbar \nabla_{r_a}, \quad M_a = g_a \frac{e_a}{2m_a} S_a, \quad c^2 \epsilon_0 \mu_0 = 1 \quad (2)$$

where

$$B(r) = i \sum_{\lambda=1,2} \int d^3k \frac{1}{c} \left( \frac{\hbar \omega(k)}{2\epsilon_0 (2\pi)^3} \right)^{1/2} (a_\lambda(k) \left( \frac{k}{|k|} \wedge \varepsilon_\lambda(k) \right) e^{ik \cdot r} - a_\lambda^*(k) \left( \frac{k}{|k|} \wedge \varepsilon_\lambda(k) \right) e^{-ik \cdot r}) \quad (3)$$

$$\Pi(r) = -i \sum_{\lambda=1,2} \int \left( \frac{\hbar \varepsilon_0 \omega(k)}{2(2\pi)^3} \right)^{1/2} (a_\lambda(k) \varepsilon_\lambda(k) e^{ik \cdot r} - a_\lambda^*(k) \varepsilon_\lambda(k) e^{-ik \cdot r}) \quad (4)$$

$$\text{and} \quad E(r) = -\frac{1}{\varepsilon_0} \Pi(r). \quad (5)$$

Here  $\omega(k) = c|k|$  and  $\varepsilon_\lambda(k)$ ,  $\lambda = 1, 2$ , are real polarization vectors satisfying

$$\varepsilon_\lambda(k) \cdot \varepsilon_\mu(k) = \delta_{\lambda\mu}, \quad k \cdot \varepsilon_\lambda(k) = 0, \quad \lambda, \mu = 1, 2 \quad (6)$$

$a_\lambda(k)$ ,  $a_\lambda^*(k)$  are the usual annihilation and creation operators obeying the canonical commutation relations

$$[a_\lambda^\sharp(k), a_\mu^\sharp(k')] = 0, \quad [a_\lambda(k), a_\mu^*(k')] = \delta_{\lambda\mu} \delta(k - k') \quad (7)$$

where  $a^\sharp = a$  or  $a^*$ .

The polarization field relative to the center-of-mass coordinate  $R$  is:

$$P(r) = \sum_{a=1}^N e_a(r_a - R) \int_0^1 d\lambda \delta(r - R_1 - \lambda(r_a - R)) \quad (8)$$

The magnetization fields relative to the center-of-mass coordinate  $R$ , for  $1 \leq a \leq N$  are

$$\Theta_a(r) = \sum_{b=1}^N e_b(r_b - R) \int_0^1 d\lambda (\lambda \delta_{ab} - \frac{m_a}{M} (\lambda - 1)) \delta(r - R_1 - \lambda(r_b - R)) \quad (9)$$

where  $R = \frac{1}{M} \sum_{a=1}^N m_a r_a$  with  $M = \sum_{a=1}^N m_a$ .

## 3 Scaling

### 3.1 General Remarks

The scaling is a change of units which exhibits the perturbative character of the different terms in the Hamiltonian that we are concerned with. Here we use dilatation of particles coordinates and photon momenta independently. Then we have to establish which terms are to be predominant in the Hamiltonian of this composite (particles and photons) system. These terms will form the zero order Hamiltonian for the perturbative expansion. In a first step, we have to determine a relevant truncated zero order Hamiltonian extending to moving atoms the properties known for non moving atoms.

In the hydrogenoid model of atoms with independent electrons, typical binding energy for each electron is of the order of  $\frac{1}{2}mc^2(Z\alpha)^2$  [M] where  $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$  is the fine structure constant,  $Z$  the nucleus charge and  $m$  the

electron mass. This quantity, which neglects all the further corrections from inter electron repulsion screening effects and exchange process, is an upper value for the total ionisation of an atom. Indeed the maximum atomic value for the first ionisation is that of the helium atom: 24.58 eV, of the order of  $(\frac{1}{2}mc^2\alpha^2Z^2)/2$ . As the multipolar formalism fits at best with confined system of charges we will disregard energies exceeding the first ionisation limit. Thus it is consistent to build a model where the Coulombic part, kinetic energy of the electrons and the free field energy have to be retained within the leading terms [FFG]. For the nuclear motion the question of the scaling factor arises: should we choose the same for nuclei and electrons? One point of view is to respect the consistency between different choices of coordinate systems for N particles systems: the natural one  $\{r_a\}_{a=[1,N]}$  and the Jacobi ones  $\{R_a\}_{a=[1,N]}$  which are generated by a definite building up of the center of mass and relative vectors and associated coordinates. As the constitutive set of equations corresponding to the transformation from one system to the other is a linear one, we have chosen to adopt a same scaling constant for nuclei and electrons in order to fit with this property.

If the nucleus is the particle  $a = 1$ , the unperturbed zero order Hamiltonian is the following one:

$$H_0 = \sum_{a=1}^N \frac{p_a^2}{2m_a} + \sum_{a=2}^N \frac{Ze^2}{4\pi\epsilon_0|r_a - r_1|} + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right), \quad (10)$$

where  $N = Z + 1$ .

### 3.2 Dilatation

We dilate the particles coordinates and photon momenta independently, *i.e.*,  $(\{r_a\}_{a=[1,N]}, k) \rightarrow \left(\left\{\frac{r_a}{\mu}\right\}_{a=[1,N]}, \eta k\right)$ ,  $\mu > 0$ ,  $\eta > 0$ , where  $\mu$  and  $\eta$  are dimensionless constants. This scaling induces a unitary transformation in the space of physical states that we now compute.

The dilation  $k \rightarrow \eta k$  induces an unitary operator in  $L^2(\mathbb{R}^3)$  denoted by  $\Gamma_\eta$  :

$$(\Gamma_\eta f)(k) = \eta^{3/2} f(\eta k), \quad \eta > 0, \quad k \in \mathbb{R}^3 \quad (11)$$

where  $f \in L^2(\mathbb{R}^3)$ .

We have for the inverse transformation

$$(\Gamma_\eta^{-1} g)(k) = \eta^{-3/2} g\left(\frac{k}{\eta}\right) \quad (12)$$

Let  $\mathcal{F}_{ph}$  be the Fock space for transversal photons.

We have  $\mathcal{F}_{ph} = \bigoplus_{n=0}^{\infty} L^2(\mathbb{R}^3, \mathcal{C}^2)^{\otimes_s n}$ , where  $L^2(\mathbb{R}^3, \mathcal{C}^2)^{\otimes_s 0} \equiv \mathcal{C}$ . Here  $L^2(\mathbb{R}^3, \mathcal{C}^2)^{\otimes_s n}$

is the symmetrized  $n$ -fold tensor product of  $L^2(\mathbb{R}^3, \mathcal{C}^2)$ . The dilation  $k \rightarrow \eta k$ ,  $\eta > 0$ , induces an unitary operator on  $\mathcal{F}_{ph}$  that we still denote by  $\Gamma_\eta$ . We have for  $\psi = (\psi^{(n)})_{n \geq 0} \in \mathcal{F}$ :

$$\begin{aligned} (\Gamma_\eta \psi)^n(k_1, \lambda_1; \dots; k_n, \lambda_n) &= \eta^{\frac{3}{2}n} \psi^{(n)}(\eta k_1, \lambda_1; \dots; \eta k_n, \lambda_n), \\ k_j &\in \mathbb{R}^3, \lambda_j = 1, 2, j = 1, \dots, n. \end{aligned} \quad (13)$$

Thus we have

$$\Gamma_\eta^{-1} a_\lambda(k) \Gamma_\eta = \eta^{3/2} a_\lambda(\eta k) \quad (14)$$

$$\Gamma_\eta^{-1} a_\lambda^*(k) \Gamma_\eta = \eta^{3/2} a_\lambda^*(\eta k) \quad (15)$$

because  $a_\lambda^*(k)$  is the adjoint of  $a_\lambda(k)$ .

The right mathematical definition of the energy operator for the photons is given by

$$\frac{1}{2} \int d^3 r : \frac{\Pi(r)^2}{\varepsilon_0} + \frac{B(r)^2}{\mu_0} : \quad (16)$$

where  $::$  is the Wick normal order (see [S]).

Let  $H_f$  denote the energy operator for the photons. We then have :

$$H_f = \frac{1}{2} \int d^3 r : \frac{\Pi(r)^2}{\varepsilon_0} + \frac{B(r)^2}{\mu_0} := \sum_{\lambda=1,2} c\hbar \int d^3 k |k| a_\lambda^*(k) a_\lambda(k). \quad (17)$$

Thus using (3), (4), (5), (19) and (14), (15) one gets:

$$\Gamma_\eta B(r) \Gamma_\eta^{-1} = \eta^2 B(\eta r), \quad (18)$$

$$\Gamma_\eta \Pi(r) \Gamma_\eta^{-1} = \eta^2 \Pi(\eta r), \quad (19)$$

$$\Gamma_\eta E(r) \Gamma_\eta^{-1} = \eta^2 E(\eta r), \quad (20)$$

$$\Gamma_\eta H_f \Gamma_\eta^{-1} = \eta H_f. \quad (21)$$

Moreover

$$\Gamma_\mu^{-1} \nabla_{r_a} \Gamma_\mu = \mu \nabla_{r_a}. \quad (22)$$

Furthermore, for any function  $V(r_a)$ , we have

$$\Gamma_\mu^{-1} V(r_a) \Gamma_\mu = V\left(\frac{r_a}{\mu}\right). \quad (23)$$

We have to transform the multipolar Hamiltonian by the total dilatation  $\Gamma$  acting both on particles coordinates and photon momenta:  $\Gamma = (\Gamma_\mu^{-1})^N \Gamma_\eta$ . Thus we now get:

$$\Gamma B(r)\Gamma^{-1} = \eta^2 B\left(\frac{\eta r}{\mu}\right), \quad (24a)$$

$$\Gamma \Pi(r)\Gamma^{-1} = \eta^2 \Pi\left(\frac{\eta r}{\mu}\right), \quad (24b)$$

$$\Gamma E(r)\Gamma^{-1} = \eta^2 E\left(\frac{\eta r}{\mu}\right), \quad (24c)$$

$$\Gamma H_f \Gamma^{-1} = \eta H_f, \quad (24d)$$

$$\Gamma p_a \Gamma^{-1} = \mu p_a, \quad (24e)$$

$$\Gamma V(r_a)\Gamma^{-1} = V\left(\frac{r_a}{\mu}\right). \quad (24f)$$

### 3.3 Determination of the common scaling constant

We first examine the action of  $\Gamma$  on the truncated Hamiltonian:

$$\begin{aligned} \Gamma H_0 \Gamma^{-1} = & \Gamma \left[ \sum_{a=1}^N \frac{1}{2m_a} (p_a)^2 + \sum_{a=2}^N \frac{Ze^2}{4\pi\epsilon_0|r_a - r_1|} + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right) \right] \Gamma^{-1} \\ & (25) \end{aligned}$$

$$= \mu^2 \sum_{a=1}^N \frac{1}{2m_a} (p_a)^2 + Z\alpha\mu \sum_{a=2}^N \frac{\hbar c}{|r_a - r_1|} + \eta \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right)$$

Choosing the kinetic energy of the electrons, the free energy of the photons and the Coulombic part as the leading terms of the same order we must have:

$$\mu^2 = Z\alpha\mu = \eta \quad (26)$$

We then get:

$$\eta = (Z\alpha)^2, \quad \mu = Z\alpha \quad \text{and} \quad \frac{\eta}{\mu} = Z\alpha \quad (27)$$

and we have:

$$\begin{aligned} \Gamma H_0 \Gamma^{-1} = & \mu^2 \left[ \sum_{a=1}^N \frac{1}{2m_a} (p_a)^2 + \sum_{a=2}^N \frac{\hbar c}{|r_a - r_1|} + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right) \right] \quad (28) \end{aligned}$$

where the electronic ground state energy corresponding to the term within brackets is  $\frac{1}{2}mc^2Z$  as  $m_a = m$  for  $a = [2, N]$ .

## 4 Scaled Multipolar expansion

### 4.1 Scaled multipolar Hamiltonian

The scaling conditions (24a – 24f, 27) and the equations (8 – 9) will now allow us to dilate all the terms of the multipolar Hamiltonian given by equation (1), once the expansion of squared bracket terms is performed.

$$\begin{aligned}
H_{mp} = & \sum_{a=1}^N \frac{1}{2m_a} p_a^2 - \sum_{a=2}^N \frac{Ze^2}{4\pi\epsilon_0|r_a - r_1|} + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right) \\
& + \sum_{2 \leq a < b} \frac{e^2}{4\pi\epsilon_0|r_a - r_b|} + \int d^3r \frac{\Pi(r) \cdot P(r)}{\epsilon_0} \\
& + \sum_{a=1}^N \frac{1}{m_a} p_a \cdot \int d^3r \Theta_a(r) \wedge B(r) - \sum_{a=1}^N M_a \cdot B(r_a) \\
& + \sum_{a=1}^N \frac{1}{2m_a} \left( \int d^3r \Theta_a(r) \wedge B(r) \right)^2 + \frac{1}{2\epsilon_0} \int d^3r P(r)^2
\end{aligned} \tag{29}$$

Constrains (26) and (27) fix the following behaviour for the involved operators:

$$\Gamma H_f \Gamma^{-1} = \mu^2 H_f, \tag{30}$$

$$\Gamma B(r) \Gamma^{-1} = \mu^4 B(\mu r), \tag{31}$$

$$\Gamma \Pi(r) \Gamma^{-1} = \mu^4 \Pi(\mu r), \tag{32}$$

$$\Gamma E(r) \Gamma^{-1} = \mu^4 E(\mu r). \tag{33}$$

Now it remains to compute the effect of the scaling transformation on terms including  $P(r)$  and  $\Theta_a(r)$  :

$$\begin{aligned}
& \Gamma \int d^3 r \frac{\Pi(r).P(r)}{\varepsilon_0} \Gamma^{-1} \\
&= \mu^3 \sum_{a=1}^N e_a(r_a - R) \cdot \int_0^1 d\lambda \int d^3 r \frac{1}{\varepsilon_0} \Pi(r) \delta(r - \mu[R - \lambda(r_a - R)]) \\
&= \mu^3 \int_0^1 d\lambda \sum_{a=1}^N e_a(r_a - R) \cdot \frac{1}{\varepsilon_0} \Pi(\mu[R - \lambda(r_a - R)]), \tag{34}
\end{aligned}$$

$$\begin{aligned}
& \Gamma \int d^3 r \Theta_a(r) \wedge B(r) \Gamma^{-1} = \mu^3 \sum_{b=1}^N e_b(r_b - R) \wedge \int_0^1 (\lambda \delta_{ab} - \frac{m_a}{M}(\lambda - 1)) \\
& \int d^3 r B(r) \delta(r - R_1 - \lambda(r_b - R)) \\
&= \mu^3 \int_0^1 d\lambda \sum_{b=1}^N (\lambda \delta_{ab} - \frac{m_a}{M}(\lambda - 1)) e_b(r_b - R) \wedge B(\mu[R - \lambda(r_b - R)]). \tag{35}
\end{aligned}$$

Finally one obtains for the multipolar Hamiltonian the following scaling:

$$\begin{aligned}
& \frac{1}{\mu^2} \Gamma H_{mp} \Gamma^{-1} = \sum_{a=1}^N \frac{1}{2m_a} p_a^2 - \sum_{a=2}^N \frac{\hbar c}{|r_a - r_1|} + \frac{1}{2} \int d^3 r \left( \frac{\Pi(r)^2}{\varepsilon_0} + \frac{B(r)^2}{\mu_0} \right) \\
& + \frac{1}{Z} \sum_{2 \leq a < b} \frac{\hbar c}{|r_a - r_b|} + \mu \int_0^1 d\lambda \sum_{a=1}^N e_a(r_a - R) \cdot \frac{1}{\varepsilon_0} \Pi(\mu[R - \lambda(r_a - R)]) \\
& - \mu^2 \sum_{a=1}^N M_a \cdot B(\mu r_a) \tag{36} \\
& + \mu^2 \int_0^1 d\lambda \sum_{a,b=1}^N (\lambda \delta_{ab} - \frac{m_a}{M}(\lambda - 1)) \frac{e_b}{m_a} \\
& (p_a \cdot ((r_b - R) \wedge B(\mu[R - \lambda(r_b - R)]))) \\
& + \mu^4 \sum_{a=1}^N \frac{1}{2m_a} \left( \int_0^1 d\lambda \sum_{b=1}^N (\lambda \delta_{ab} - \frac{m_a}{M}(\lambda - 1)) e_b \right. \\
& \left. (r_b - R) \wedge B(\mu[R - \lambda(r_b - R)]) \right)^2 \\
& = \frac{1}{\mu^2} \Gamma H_0 \Gamma^{-1} + \frac{1}{\mu^2} \Gamma H_{mp}^I \Gamma^{-1}.
\end{aligned}$$

As usual the vacuum polarization term, which scales as  $\mu^{-2}$  has been forgotten in (36), and the last equality defines  $H_{mp}^I$ .



## 4.2 Multipolar expansions

The multipolar expansion of the expression (36) is straightforward. It relies on the usual Taylor series expansion for  $F = B$  or  $\Pi$ :

$$F(\mu[R - X]) = \sum_{n=0}^{\infty} \mu^n \frac{(X \cdot \nabla_r)^n}{n!} F(r)|_{r=\mu R} \quad (37)$$

where  $X$  stands for  $(r - R_a)$  or  $\lambda(r_a - R)$ .

Note that  $|k| |r_\alpha - R|$  is of the order of  $|k| a_1(Z)$  where  $a_1(Z) = mcZ\alpha/\hbar$ . As the photons energy has to be lower to the value  $mc^2$  which is used for the ultraviolet cutoff [BFS], it then results that  $|k| < mc/\hbar$ . Therefore the  $\mu |k \cdot (r_a - R)|$  factor in the exponential terms of the field expansions (3) and (4) can be assumed to be small (mod  $2\pi$ ).

One then gets the following explicit  $\mu$ -expansions for these terms.

**Electric multipole terms:**

$$\begin{aligned} & \mu \int_0^1 d\lambda \sum_{\alpha=1}^N e_\alpha(r_\alpha - R) \cdot \frac{1}{\varepsilon_0} \Pi(\mu[R - \lambda(r_\alpha - R)]) \\ &= \sum_{n=0}^{\infty} \mu^{n+1} \sum_{\alpha=1}^N e_\alpha(r_\alpha - R) \cdot \frac{((r_\alpha - R) \cdot \nabla_r)^n \Pi(r)|_{r=\mu R}}{(n+1)! \varepsilon_0} \\ &= \sum_{n=0}^{\infty} \mu^{n+1} T_E^n(\mu) \end{aligned} \quad (38)$$

**Spin multipole terms**

$$\begin{aligned} & \mu^2 \sum_{\alpha=1}^N M_\alpha \cdot B(\mu r_\alpha) \\ &= \sum_{n=0}^{\infty} \mu^{n+2} (-1)^n \sum_{\alpha=1}^N M_\alpha \cdot \frac{((r_\alpha - R) \cdot \nabla_r)^n B(r)|_{r=\mu R}}{n!} \\ &= \sum_{n=0}^{\infty} \mu^{n+2} T_S^n(\mu) \end{aligned} \quad (39)$$

### Magnetic multipole terms

$$\begin{aligned}
& \mu^2 \int_0^1 d\lambda \sum_{\alpha, \beta=1}^N (\lambda \delta_{\alpha\beta} - \frac{m_\alpha}{M}(\lambda - 1)) \frac{e_\beta}{m_\alpha} \\
& (p_\alpha \cdot ((r_\beta - R) \wedge B(\mu[R - \lambda(r_\beta - R)]))) \\
& = \sum_{n=0}^{\infty} \mu^{n+2} \left\{ \int_0^1 d\lambda \sum_{\alpha, \beta=1}^N \lambda^n (\lambda \delta_{\alpha\beta} - \frac{m_\alpha}{M}(\lambda - 1)) \right. \\
& \left. \frac{e_\beta}{m_\alpha} \left( p_\alpha \cdot \left( (r_\beta - R) \wedge \frac{((r_\alpha - R) \cdot \nabla_r)^n}{n!} B(r)|_{r=\mu R} \right) \right) \right\} \\
& = \sum_{n=0}^{\infty} \mu^{n+2} T_M^n(\mu)
\end{aligned} \tag{40}$$

### Diamagnetic multipole terms

$$\begin{aligned}
& \mu^4 \sum_{\alpha=1}^N \frac{1}{2m_\alpha} \left( \int_0^1 d\lambda \sum_{\beta=1}^N (\lambda \delta_{\alpha\beta} - \frac{m_\alpha}{M}(\lambda - 1)) e_\beta \right. \\
& \left. (r_\beta - R) \wedge B(\mu[R - \lambda(r_\beta - R)]) \right)^2 \\
& = \mu^4 \sum_{\alpha=1}^N \frac{1}{2m_\alpha} \left\{ \int_0^1 d\lambda \sum_{\beta=1}^N \sum_{n=0}^{\infty} \right. \\
& \left. \mu^n \lambda^n (\lambda \delta_{\alpha\beta} - \frac{m_\alpha}{M}(\lambda - 1)) e_\beta \left( (r_\beta - R) \wedge \frac{((r_\alpha - R) \cdot \nabla_r)^n}{n!} B(r)|_{r=\mu R} \right) \right\}^2 \\
& = \sum_{n=0}^{\infty} \mu^{n+4} T_{MM}^n(\mu)
\end{aligned} \tag{41}$$

This allows to perform direct expansion up to the required order in  $\mu = Z\alpha$  of the multipolar Hamiltonian for an atom considered as a confined neutral system of charges. Assuming that  $T_E^n, T_S^n, T_M^n, T_{MM}^n = 0$  for  $n < 0$ , one gets for the interaction Hamiltonian  $H_{mp}^I$  the following multipolar expansion:

$$\frac{1}{\mu^2} \Gamma H_{mp}^I \Gamma^{-1} = \sum_{n=0}^{\infty} \mu^n \{ T_E^{n-1}(\mu) + T_S^{n-2}(\mu) + T_M^{n-2}(\mu) + T_{MM}^{n-4}(\mu) \} \tag{42}$$

### 4.3 Multipolar expansion of the minimal coupling Hamiltonian.

For sake of completeness let us remind the expression of the minimal coupling Hamiltonian corresponding to the same system of charges as in (1):

$$\begin{aligned}
H_{mc} = & \sum_{\alpha=1}^N \frac{1}{2m_{\alpha}} (p_{\alpha} - e_{\alpha}A(r))^2 + \sum_{\alpha < \beta} \frac{e_{\alpha}e_{\beta}}{4\pi\epsilon_0|r_{\alpha} - r_{\beta}|} \\
& - \sum_{\alpha=1}^N M_{\alpha} \cdot B(r_{\alpha}) + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right),
\end{aligned} \tag{43}$$

where

$$A(r) = \sum_{\lambda=1,2} \int d^3k \left( \frac{\hbar}{2\epsilon_0 (2\pi)^3 \omega(k)} \right)^{\frac{1}{2}} \epsilon_{\lambda}(k) \left\{ a_{\lambda}(k) e^{ik \cdot r} + a_{\lambda}^*(k) e^{-ik \cdot r} \right\} \tag{44}$$

One easily computes that  $\Gamma A(r) \Gamma^{-1} = \mu^2 A(\mu r)$ . For the other terms the preceding analysis remains unchanged. As a result one gets a scaled expression for the minimal coupling Hamiltonian:

$$\begin{aligned}
\frac{1}{\mu^2} \Gamma H_{mc} \Gamma^{-1} = & \sum_{\alpha=1}^N \frac{1}{2m_{\alpha}} p_{\alpha}^2 - \sum_{\alpha=2}^N \frac{\hbar c}{|r_{\alpha} - r_1|} + \frac{1}{2} \int d^3r \left( \frac{\Pi(r)^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right) \\
& + \frac{1}{Z} \sum_{2 \leq \alpha < \beta} \frac{\hbar c}{|r_{\alpha} - r_{\beta}|} - \mu \sum_{\alpha=1}^N \frac{e_{\alpha}}{m_{\alpha}} p_{\alpha} \cdot A(\mu r_{\alpha}) \\
& - \mu^2 \sum_{\alpha=1}^N M_{\alpha} \cdot B(\mu r_{\alpha}) + \mu^2 \sum_{\alpha=1}^N \frac{e_{\alpha}^2}{2m_{\alpha}} A(\mu r_{\alpha})^2 \\
= & \frac{1}{\mu^2} \Gamma H_0 \Gamma^{-1} + \frac{1}{\mu^2} H_{mc}^I \Gamma^{-1},
\end{aligned} \tag{45}$$

where the right hand side defines  $H_{mc}^I$ .

The multipolar expansion is the consequence of (37) for  $F = A$  and  $X = (r - R_a)$ :

$$\begin{aligned}
& \mu \sum_{\alpha=1}^N \frac{e_{\alpha}}{m_{\alpha}} p_{\alpha} \cdot A(\mu r_{\alpha}) \\
= & \sum_{n=0}^{\infty} \mu^{n+1} (-1)^n \sum_{\alpha=1}^N \frac{e_{\alpha}}{m_{\alpha}} p_{\alpha} \cdot \frac{((r_{\alpha} - R) \cdot \nabla_r)^n}{n!} A(r)|_{r=\mu R} \\
= & \sum_{n=0}^{\infty} \mu^{n+1} T_A^n(\mu).
\end{aligned} \tag{46}$$

and

$$\begin{aligned}
\mu^2 \sum_{\alpha=1}^N \frac{e_\alpha^2}{2m_\alpha} A(\mu r_\alpha)^2 &= \sum_{n=0}^{\infty} \mu^{n+2} \times \\
\sum_{l=0}^n \sum_{\alpha=1}^N \frac{e_\alpha^2}{2m_\alpha} \frac{((r_\alpha - R) \cdot \nabla_r)^{n-l}}{(n-l)!} A(r)|_{r=\mu R} \cdot \frac{((r_\alpha - R) \cdot \nabla_r)^l}{l!} A(r)|_{r=\mu R} &\quad (47) \\
&= \sum_{n=0}^{\infty} \mu^{n+2} T_{AA}^n(\mu).
\end{aligned}$$

Assuming that  $T_A^n, T_{AA}^n = 0$  for  $n < 0$ , one gets for the minimal coupling interaction Hamiltonian the following expansion:

$$\frac{1}{\mu^2} \Gamma H_{mc}^I \Gamma^{-1} = \sum_{n=0}^{\infty} \mu^n \{ T_A^{n-1}(\mu) + T_S^{n-2}(\mu) + T_{AA}^{n-2}(\mu) \} \quad (48)$$

Thus the correspondence between terms of the same order in  $\mu$  for  $H_{mp}$  and  $H_{mc}$  can be established by direct comparison of the expressions (36) and (43) or (42) and (48) with multipolar expansions given by (38,39,40,41,46,47).

## 5 Explicit Expansions for atoms with 1,2,3 electrons

### 5.1 Jacobi vectors

As the center of mass vector  $R$  and the  $\{r_a\}_{1 \leq a \leq N}$  are linearly dependent, one has to consider Jacobi vectors  $\{R_a\}_{1 \leq a \leq N}$  in order to use independent variables. They are many such families of vectors, each one being related to a definite building of the center of mass which has to preserve the quantity  $I = \sum_\alpha m_\alpha r_\alpha^2 = \sum_\alpha M_\alpha R_\alpha^2$ , where  $(\sum_\alpha m_\alpha) R_1 = \sum_\alpha m_\alpha r_\alpha$ ,  $M_1 = (\sum_\alpha m_\alpha)$  and  $M_\alpha$  is the effective mass corresponding to the associated  $R_\alpha$ . Usually one proceeds imaging what is done for two particles, pairing center of mass of (effective) particles getting at each step the center of mass, the relative vector and the associated masses.

### 5.2 Octupole approximation for a neutral two body system

We consider here the hydrogen atom. Here,  $e_1 = e$ ,  $e_2 = -e$ . We introduce the Jacobi vectors  $\{R_\alpha\}_{\alpha=1,2}$ .

We set

$$\begin{aligned}
R_2 &= r_1 - r_2, \quad \frac{1}{M_2} = \frac{1}{m_1} + \frac{1}{m_2}, \quad R_1 = \frac{m_1 r_1 + m_2 r_2}{M}, \\
M_1 &= m_1 + m_2, \quad P_1 = -i\hbar \nabla_{R_1}, \quad P_2 = -i\hbar \nabla_{R_2}.
\end{aligned}$$

We obtain

$$\begin{cases} r_1 = R_1 + \frac{m_2}{M_1} R_2, \\ r_2 = R_1 - \frac{m_1}{M_1} R_2 \end{cases}, \quad \begin{cases} p_1 = P_2 + \frac{m_1}{M_1} P_1, \\ p_2 = -P_2 + \frac{m_2}{M_1} P_1. \end{cases}$$

In this new system of coordinates,  $H_{mp}$  is given by:

$$H_{mp} = H_0 + W_e, \quad (49)$$

where

$$\begin{aligned} H_0 &= \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} - \frac{e^2}{4\pi\epsilon_0|R_2|} + H_f, \\ W_e &= H_{mp} - H_0. \end{aligned}$$

Thus, letting  $\mu = \alpha$  in (38 – 42) the octupole approximation of  $\frac{1}{\mu^2}\Gamma H_{mp}\Gamma^{-1}$  is given by:  $H_0 + W'_\mu$ ,  
where

$$H_0 = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} - \frac{\hbar c}{|R_2|} + H_f, \quad (50)$$

and

$$W'_\mu = \mu W_\mu^1 + \mu^2 W_\mu^2 + \mu^3 W_\mu^3 + \mu^4 W_\mu^4, \quad (51)$$

with

$$\begin{aligned} W_\mu^1 &= -T_E^0(\mu) = -eR_2.E(\alpha R_1), \\ W_\mu^2 &= -T_S^0(\mu) + T_M^0(\mu) + T_E^1(\mu) \\ &= -(M_1 + M_2).B(\alpha R_1) + \frac{1}{2M_1}[P_1.eR_2 \wedge B(\alpha R_1) + h.c] \\ &\quad + \frac{1}{4M_1}(1 - \frac{4M_2}{M_1})^{\frac{1}{2}}[P_2.eR_2 \wedge B(\alpha R_1) + h.c] \\ &\quad - \frac{1}{2}(1 - \frac{4M_2}{M_1})^{\frac{1}{2}}eR_2.(R_2.\nabla_r)E(r)|_{r=\alpha R_1}, \\ W_\mu^3 &= T_M^1(\mu) + T_E^2(\mu) \\ &= \frac{1}{4M_1}(1 - \frac{4M_2}{M_1})^{\frac{1}{2}}[P_1.eR_2 \wedge (R_2.\nabla_r)B(r)|_{r=\alpha R_1} + h.c] \\ &\quad + \frac{1}{6M_2}(1 - \frac{3M_2}{M_1})[P_2.eR_2 \wedge (R_2.\nabla_r)B(r)|_{r=\alpha R_1} + h.c] \\ &\quad - \frac{1}{6}(1 - \frac{3M_2}{M_1})eR_2.(R_2.\nabla_r)^2E(r)|_{r=\alpha R_1}, \end{aligned} \quad (52)$$

$$\begin{aligned}
W_\mu^4 &= T_M^2(\mu) + T_E^3(\mu) + T_{MM}^0(\mu) \\
&= \frac{1}{12M_1} \left(1 - \frac{3M_2}{M_1}\right) [P_1 \cdot eR_2 \wedge (R_2 \cdot \nabla_r)^2 B(r)|_{r=\alpha R_1} + h.c] \\
&\quad + \frac{M^3}{2M_2} \left(1 - \frac{4M_2}{M_1}\right)^{\frac{1}{2}} \left(1 - \frac{2M_2}{M_1}\right) [P_2 \cdot eR_2 \wedge (R_2 \cdot \nabla_r)^2 B(r)|_{r=\alpha R_1} + h.c] \quad (53) \\
&\quad - \frac{1}{24} \left(1 - \frac{4M_2}{M_1}\right)^{\frac{1}{2}} \left(1 - \frac{2M_2}{M_1}\right) eR_2 \cdot (R_2 \cdot \nabla_r)^3 E(r)|_{r=\alpha R_1} \\
&\quad + \frac{1}{8M_2} (eR_2 \wedge B(\alpha R_1))^2.
\end{aligned}$$

Let us remark that, at the second order in  $\mu$ , the term  $R_2 \cdot (R_2 \cdot \nabla_r) E(r)|_{r=\mu R_1}$  does not appear in [GR] because the authors only consider the dipolar approximation. The quadrupolar electric term appears as soon as one considers the quadrupolar approximation.

### 5.3 Quadrupole-approximation for a neutral three-body system

Now we consider a neutral 3 body system as, for example, the helium atom  $He^4$ . Let  $H_{mp}^{He}$  be the Hamiltonian of the considered system.

Consider a system formed of 3 particles  $A_1, A_2, A_3$  of respective masses  $m_1, m_2, m_3$ , with charges  $e_1, e_2, e_3$ , of positions  $r_1, r_2, r_3$  and of impulsion  $p_1, p_2, p_3$ .

We introduce the Jacobi vectors associated to the following partition:  $a = \{(1, 2), 3\}$ . It is the case of a neutral atom formed of a nucleus of charge  $-2e$  and of two electrons each one having a charge  $e$ .

We set

$$\begin{aligned}
R_2 &= r_2 - r_1, \quad R_1 = \frac{m_1 r_1 + m_2 r_2 + m_3 r_3}{M_1}, \quad M_1 = m_1 + m_2 + m_3 \\
R_3 &= r_3 - \frac{m_1 r_1}{M_2} - \frac{m_2 r_2}{m}, \quad M_2 = m_1 + m_2. \\
P_1 &= -i\hbar \nabla_{R_1}, \quad P_2 = -i\hbar \nabla_{R_2}, \quad P_3 = -i\hbar \nabla_{R_3}.
\end{aligned}$$

We obtain

$$\begin{cases} r_1 = R_1 - \frac{m_3}{M_1} R_3 - \frac{m_2}{M_2} R_2 \\ r_2 = R_1 - \frac{m_3}{M_1} R_3 + \frac{m_1}{M_2} R_2 \\ r_3 = R_1 + \frac{M_2}{M_1} R_3 \end{cases}, \quad \begin{cases} p_1 = \frac{m_1}{M_1} P_1 - \frac{m_1}{M_2} P_3 - P_2 \\ p_2 = \frac{m_2}{M_1} P_1 - \frac{m_2}{M_2} P_3 + P_2 \\ p_3 = \frac{m_3}{M_1} P_1 + P_3 + P_2 \end{cases}$$

In the case of the Helium atom we have  $m_1 = m_2, e_1 = e_2 = e$  and  $e_3 = -2e$ .

In this new system of coordinates,  $H_{mp}^{He}$  is given by:

$$\begin{aligned}
H_{mp}^{He} = & \frac{1}{2m_1} \left[ \frac{m_1}{M_1} P_1 - \frac{1}{2} P_3 - P_2 + \int_{\mathbb{R}^3} \Theta_1(r) \wedge B(r) d^3 r \right]^2 \\
& + \frac{1}{2m_1} \left[ \frac{m_1}{M_1} P_1 - \frac{1}{2} P_3 + P_2 + \int_{\mathbb{R}^3} \Theta_2(r) \wedge B(r) d^3 r \right]^2 \\
& + \frac{1}{2m_3} \left[ \frac{m_3}{M_1} P_1 + P_3 + \int_{\mathbb{R}^3} \Theta_3(r) \wedge B(r) d^3 r \right]^2 \\
& + \frac{e^2}{4\pi\varepsilon_0|R_2|} - \frac{2e^2}{4\pi\varepsilon_0|R_3 + \frac{1}{2}R_2|} - \frac{2e^2}{4\pi\varepsilon_0|R_3 - \frac{1}{2}R_2|} \\
& - \sum_{\alpha=1}^3 M_\alpha \cdot B(r_\alpha) + H_f - \int_{\mathbb{R}^3} E(r) \cdot P(r) d^3 r.
\end{aligned}$$

We write  $H_{mp}^{He}$  under the following form:

$$H_{mp}^{He} = H_0^{He} + W_e,$$

with

$$\begin{aligned}
H_0^{He} : = & \frac{P_1^2}{2M_1} + \frac{P_3^2}{2\mu_{12,3}} + \frac{P_2^2}{2m_1} + \frac{e^2}{4\pi\varepsilon_0|R_2|} - \frac{2e^2}{4\pi\varepsilon_0|R_3 + \frac{1}{2}R_2|} \\
& - \frac{2e^2}{4\pi\varepsilon_0|R_3 - \frac{1}{2}R_2|} + H_f,
\end{aligned} \tag{54}$$

and

$$W_e := H_{mp}^{He} - H_0^{He}.$$

Here  $\frac{1}{\mu_{12,3}} = \frac{1}{2m_1} + \frac{1}{m_3}$ .

Letting  $N = 3$  in (38 – 42) we get at the second order in  $\mu = 2\alpha$ :

$$H_\mu^Q = \frac{1}{\mu^2} \Gamma H_{mp}^{He} \Gamma^{-1} = H_0^{He} + W_\mu, \tag{55}$$

where,

$$H_0^{He} = \frac{P_1^2}{2M_1} + \frac{P_3^2}{2\mu_{12,3}} + \frac{P_2^2}{m_1} + \frac{\hbar c}{2|R_2|} - \frac{\hbar c}{|R_3 + \frac{1}{2}R_2|} - \frac{\hbar c}{|R_3 - \frac{1}{2}R_2|} + H_f, \tag{56}$$

$$W_\mu = \mu W_\mu^1 + \mu^2 W_\mu^2, \tag{57}$$

with

$$\begin{aligned}
W_\mu^1 &= -T_E^0(\mu) = 2eR_3.E(2\alpha R_1), \\
W_\mu^2 &= -T_S^0(\mu) + T_M^0(\mu) + T_E^1(\mu) \\
&= -(M_1 + M_2 + M_3).B(2\alpha R_1) - \frac{1}{M_1}[P_1.eR_3 \wedge B(2\alpha R_1) + h.c] \\
&+ \frac{1}{2\mu_{12,3}}(1 - \frac{4\mu_{12,3}}{M_1})^{\frac{1}{2}}[P_3.eR_3 \wedge B(2\alpha R_1) + h.c] \\
&+ \frac{1}{4m_1}[P_2.eR_2 \wedge B(2\alpha R_1) + h.c] \\
&- e[(1 - \frac{4\mu_{12,3}}{M_1})^{\frac{1}{2}}R_3.(R_3.\nabla_r) + \frac{1}{4}R_2.(R_2.\nabla_r)]E(r)|_{r=2\alpha R_1}.
\end{aligned} \tag{58}$$

#### 5.4 Quadrupole-approximation for a neutral four-body system

We are finally interested in the case of neutral moving system formed of four bodies. For this system we consider the following partition for  $\{1, 2, 3, 4\}$  :

$$c = \{a, 4\}, \quad a = \{1, 2, 3\}.$$

This partition correspond to the lithium atom.

We define the Jacobi vectors as follows:

$$\begin{aligned}
R_2 &= r_1 - r_2, \quad R_3 = r_3 - \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2}, \quad R_4 = (R_4, R_3) \\
R_4 &= r_4 - \frac{m_1 r_1 + m_2 r_2 + m_3 r_3}{m_1 + m_2 + m_3}, \quad M_4 = m_1 + m_2 + m_3 \\
R_1 &= \frac{m_1 r_1 + m_2 r_2 + m_3 r_3 + m_4 r_4}{M}, \quad M_1 = m_1 + m_2 + m_3 + m_4
\end{aligned}$$

$$P_2 = -i\hbar\nabla_{R_2}, \quad P_3 = -i\hbar\nabla_{R_3}, \quad P_4 = -i\hbar\nabla_{R_4}, \quad P_1 = -i\hbar\nabla_{R_1}.$$

We suppose here that  $m_1 = m_2 = m_3$  and we set  $m_1 = m_2 = m_3$  and  $m_4 = m_2$ .

We then obtain

$$\begin{cases} r_1 = R_1 - \frac{m_2}{M_1}R_4 - \frac{1}{3}R_3 + \frac{1}{2}R_2 \\ r_2 = R_1 - \frac{m_2}{M_1}R_4 - \frac{1}{3}R_3 - \frac{1}{2}R_2 \\ r_3 = R_1 - \frac{m_2}{M_1}R_4 - \frac{2}{3}R_3 \\ r_4 = R_1 + \frac{m_2}{M_1}R_4 \end{cases}, \quad \begin{cases} p_1 = \frac{m_1}{M_1}P_1 - \frac{1}{3}P_4 - \frac{1}{2}P_3 + P_2 \\ p_2 = \frac{m_1}{M_1}P_1 - \frac{1}{3}P_4 - \frac{1}{2}P_3 - P_2 \\ p_3 = \frac{m_1}{M_1}P_1 - \frac{1}{3}P_4 + P_3 \\ p_4 = \frac{m_2}{M_1}P_1 + P_4. \end{cases}$$



We recall that the Hamiltonian  $H_{mp}^{Li}$  of the considered system is given by:

$$\begin{aligned} H_{mp}^{Li} &= \sum_{\alpha=1}^4 \frac{1}{2m_{\alpha}} (p_{\alpha} + \int d^3r \Theta_{\alpha}(r) \wedge B(r))^2 + \sum_{1 \leq \alpha < \beta \leq 4} \frac{e_{\alpha} e_{\beta}}{4\pi\epsilon_0 |r_{\alpha} - r_{\beta}|} \\ &- \sum_{\alpha=1}^4 M_{\alpha} \cdot B(r_{\alpha}) + \frac{1}{2} \int d^3r \left( \frac{(\Pi(r) + P(r))^2}{\epsilon_0} + \frac{B(r)^2}{\mu_0} \right). \end{aligned}$$

We now consider that  $e_1 = e_2 = e_3 = e$  and  $e_4 = -3e$ , the lithium atom.

In the new system of coordinates the Hamiltonian  $H_{mp}^{Li}$  is written as follows:

$$\begin{aligned} H_{mp}^{Li} &= \frac{1}{2m_1} \left( \frac{m_1}{M_1} P_1 - \frac{1}{3} P_4 - \frac{1}{2} P_3 + P_2 + \int d^3r \Theta_1(r) \wedge B(r) \right)^2 \\ &+ \frac{1}{2m_1} \left( \frac{m_1}{M_1} P_1 - \frac{1}{3} P_4 - \frac{1}{2} P_3 - P_2 + \int d^3r \Theta_2(r) \wedge B(r) \right)^2 \\ &+ \frac{1}{2m_1} \left( \frac{m_1}{M_1} P_1 - \frac{1}{3} P_4 + P_3 + \int d^3r \Theta_3(r) \wedge B(r) \right)^2 \\ &+ \frac{1}{2m_2} \left( \frac{m_2}{M_1} P_1 + P_4 + \int d^3r \Theta_4(r) \wedge B(r) \right)^2 \\ &+ \frac{e^2}{4\pi\epsilon_0 |R_2|} + \frac{e^2}{4\pi\epsilon_0 |R_3 - \frac{1}{2}R_2|} + \frac{e^2}{4\pi\epsilon_0 |R_3 + \frac{1}{2}R_2|} \\ &- \frac{3e^2}{4\pi\epsilon_0 |R_4 + \frac{1}{3}R_3 - \frac{1}{2}R_2|} - \frac{3e^2}{4\pi\epsilon_0 |R_4 + \frac{1}{3}R_3 + \frac{1}{2}R_2|} \\ &- \frac{3e^2}{4\pi\epsilon_0 |R_4 - \frac{2}{3}R_3|} + H_f - \sum_{\alpha=1}^4 M_{\alpha} \cdot B(r_{\alpha}) - \int E(r) \cdot P(r) d^3r. \end{aligned}$$

We then write under the following form:

$$H_{mp}^{Li} = H_0^{Li} + W_e,$$

where

$$\begin{aligned} H_0^{Li} &= \frac{P_1^2}{2M_1} + \frac{M_1}{6m_1m_2} (P_4)^2 + \frac{3}{4m_1} (P_3)^2 + \frac{1}{m_1} P_2^2 \\ &+ \frac{e^2}{4\pi\epsilon_0 |R_2|} + \frac{e^2}{4\pi\epsilon_0 |R_3 - \frac{1}{2}R_2|} + \frac{e^2}{4\pi\epsilon_0 |R_3 + \frac{1}{2}R_2|} \\ &- \frac{3e^2}{4\pi\epsilon_0 |R_4 + \frac{1}{3}R_3 - \frac{1}{2}R_2|} - \frac{3e^2}{4\pi\epsilon_0 |R_4 + \frac{1}{3}R_3 + \frac{1}{2}R_2|} \\ &- \frac{3e^2}{4\pi\epsilon_0 |R_4 - \frac{2}{3}R_3|} + H_f, \end{aligned} \tag{59}$$

and

$$\begin{aligned}
W_e = & - \sum_{\alpha=1}^4 M_{\alpha} \cdot B(R_1) - \int E(r) \cdot P(r) d^3r \\
& + \frac{1}{2M_1} (P_1 \cdot \int d^3r (\sum_{j=1}^4 \Theta_j(r) \wedge B(r) + \int d^3r (\sum_{j=1}^4 \Theta_j(r) \wedge B(r) \cdot P_1) \\
& - \frac{1}{6m_1} (P_4 \cdot \int d^3r (\sum_{j=1}^3 \Theta_j(r) \wedge B(r) + \int d^3r (\sum_{j=1}^3 \Theta_j(r) \wedge B(r) \cdot P_4) \\
& + \frac{1}{2m_2} (P_4 \cdot \int d^3r \Theta_4(r) \wedge B(r) + \int d^3r \Theta_4(r) \wedge B(r) \cdot P_4) \\
& - \frac{1}{4m_1} (P_3 \cdot \int d^3r (\Theta_1(r) + \Theta_2(r) - 2\Theta_3(r)) \wedge B(r) \tag{60} \\
& + \int d^3r (\Theta_1(r) + \Theta_2(r) - 2\Theta_3(r)) \wedge B(r) \cdot P_3) \\
& + \frac{1}{2m_1} (P_2 \cdot \int d^3r (\Theta_1(r) - \Theta_2(r)) \wedge B(r) \\
& + \int d^3r (\Theta_1(r) - \Theta_2(r)) \wedge B(r) \cdot P_2) \\
& + \frac{1}{2m_1} \{ (\int d^3r \Theta_1(r) \wedge B(r))^2 + (\int d^3r \Theta_2(r) \wedge B(r))^2 \} \\
& + \frac{1}{2m_1} (\int d^3r \Theta_3(r) \wedge B(r))^2 + \frac{1}{2m_2} (\int d^3r \Theta_4(r) \wedge B(r))^2.
\end{aligned}$$

Let

$$H_{\mu}^{Li} = \frac{1}{\mu^2} \Gamma H_{mp}^{Li} \Gamma^{-1}. \tag{61}$$

Setting  $N = 4$  in (38 – 42) we obtain at the second order in  $\mu = 3\alpha$ :

$$H_{\mu}^{Li} = H_0^{Li} + \mu W_{\mu}^1 + \mu^2 W_{\mu}^2, \tag{62}$$

with

$$\begin{aligned}
H_0^{Li} = & \frac{P_1^2}{2M_1} + \frac{M_1}{6m_1 m_2} P_4^2 + \frac{3}{4m_1} P_3^2 + \frac{1}{m_1} P_2^2 \\
& + \frac{\hbar c}{|R_2|} + \frac{\hbar c}{|R_3 - \frac{1}{2}R_2|} + \frac{\hbar c}{|R_3 + \frac{1}{2}R_2|} \tag{63} \\
& - \frac{3\hbar c}{|R_4 + \frac{1}{3}R_3 - \frac{1}{2}R_2|} - \frac{3\hbar c}{|R_4 + \frac{1}{3}R_3 + \frac{1}{2}R_2|} - \frac{3\hbar c}{|R_4 - \frac{2}{3}R_3|} + H_f,
\end{aligned}$$

$$\begin{aligned}
W_\mu^1 &= -T_E^0(\mu) = -3eR_4.E(3\alpha R_1), \\
W_\mu^2 &= -T_S^0(\mu) + T_M^0(\mu) + T_E^1(\mu) \\
&= -[M_1 + M_2 + M_3 + M_4].B(3\alpha R_1) \\
&\quad + \left[ \frac{3(m_2 - 3m_1)e}{2M_1} R_4.(R_4.\nabla_r) + \frac{e}{3} R_3.(R_3.\nabla_r) + \frac{e}{4} R_2.(R_2.\nabla_r) \right]. \\
&\quad E(r)|_{r=3\alpha R_1} \\
&\quad + \frac{1}{2M_1} [P_1.d \wedge B(3\alpha R_1) + h.c] + \frac{1}{12} [P_4.d \wedge B(3\alpha R_1) + h.c] \\
&\quad + \frac{1}{4m_1} [P_3.eR_3 \wedge B(3\alpha R_1) + h.c] + \frac{1}{4m_1} [P_2.eR_2 \wedge B(3\alpha R_1) + h.c].
\end{aligned} \tag{64}$$

We observe that the several approximations for the neutral composite systems of 2, 3 and 4 particles we have obtained are exactly the same as the ones got by [F]. In [F] the author first computes the multipolar expansion and then implements the scaling analysis.

## 6 Conclusion:

We have found again (see [GR]) the electric dipolar term at first order in  $\mu$  and at second order in  $\mu$  the magnetic dipolar term together with the Röntgen one that already appear in the dipolar approximation of  $H_{mp}$ . But now, considering the full multipolar expansion in  $\mu$ , we have shown that an extra term, i.e., an electric quadrupolar term appears also at the second order in  $\mu$ .

This strongly suggests that we must finally consider in energy computation the following Hamiltonian instead of the usual dipolar one:

$$H_{mp}^{(2)} = H_0 + (-T_E^0 + \{-T_S^0 + T_M^0 + T_E^1\}). \tag{65}$$

As the symmetries of the involved terms are different, a new level of complexity has to be taken into account. For instance for the computation of the spontaneous emission of these atomic system, the deductions of [WB] have to be consider again.

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